



DOI: 10.5281/zenodo.258087

# **COROPLASTIC ART IN SICILY: AN INVESTIGATION ON PROVENANCE AND MANUFACTURING TECHNOLOGY OF GREEK ARCHITECTURAL TERRACOTTAS FROM GELA (ITALY)**

**G. Barone<sup>1</sup>, P. Mazzoleni<sup>1</sup>, S. Raneri<sup>1</sup>, G. Spagnolo<sup>2</sup>, A. Santostefano<sup>2</sup>**<sup>1</sup> *Department of Biological, Geological and Environmental Sciences, University of Catania, C.so Italia 57,  
95129 Catania, Italy*<sup>2</sup> *Department of Ancient and Modern Civilizations, University of Messina, Polo Universitario Annunziata,  
98168 Messina, Italy***Received: 18/07/2016****Accepted: 15/12/2016***Corresponding author: Paolo Mazzoleni ([pmazzol@unict.it](mailto:pmazzol@unict.it))*

## **ABSTRACT**

In the 6<sup>th</sup> and 5<sup>th</sup> centuries B.C., Gela (Italy, Sicily) was one of the most important production centres of architectural terracottas in the Mediterranean basin. Nevertheless, few archaeometric data are actually available in scientific literature on this interesting artifacts class.

Here we report an archaeometric characterization of Geloan coroplastic materials. In particular, an investigation on finest architectural terracottas found in dumps archaeological contexts in Gela has been carried out with the aim at identifying the distinctive features of the production and the manufacturing techniques. The group of samples includes various remarkable architectural elements: painted sima and geison fragments, and acroteria specimens.

Information about provenance, fabric features, technology and manufacturing techniques have been obtained by performing petrographic (OM), mineralogical (XRD) and chemical analyses (XRF). Moreover, as most of the identified petrographic fabrics have revealed the presence of volcanic temper, EDS chemical analysis have been performed on clinopiroxenes, being the latter ones an effective tool for provenance attributions. Finally, an analytical characterization of the painted polychrome decoration has been carried out by using Scanning Electron Microscopy coupled with Energy-Dispersive Spectrometry (SEM-EDS) and micro Raman spectroscopy.

The obtained results allow us to define, for the first time, the technological features of the Geloan architectural terracottas production, opening new perspectives in the study of the coroplastic art in archaic Sicily.

---

**KEYWORDS:** Roof revetments, coroplastic art, Sicily, Gela, terracottas, archaic age

---

## 1. INTRODUCTION

In the archaic and classical period, Greeks usually protected the wooden roofs of the monumental buildings with terracotta revetments. Along with acroteria on top of the roofs, these revetments had also the function of decorating the temples.

According to scholars, Gela (Italy), an important Greek colony founded in the early 7th century B.C. on the Southern coast of Sicily, was one of the main centres of production of architectural terracottas in the Mediterranean basin in the 6th and 5th centuries B.C., since a large amount of very refined roof revetments and acroteria fragments have been found in the city. The archeological interpretations also suggest that, at the beginning of the 6th century B.C., the Geloan artisans (or at least the Syracusan ones) invented a specific style of roof revetment, today known as "Sicilian system", which quickly became very popular in Sicily and (Wikander, 1986; Winter, 1993). In fact, during the 6th century B.C., this system was employed in the temples of both Gela and Syracuse, as well as in the famous Treasury of Gela in the Panhellenic sanctuary of Olympia (Schleif and Süserott, 1944; Mallwitz, 1972; Mertens-Horn, 1990; Heiden, 1995). On the other hand, the hypothesis of high-specialized local workshops of architectural revetments and decorations at Gela accords well with the clear archaeological evidences of a local rich production of potteries (Adamesteanu, 1954, 1956a; De Miro and Fiorentini, 1983) and terracotta figurines (Sguaitamatti, 1984; Uhlenbrock, 1988; Spagnolo, 2000).

The "Sicilian" roof revetment system was characterized by specific features as the profile of its architectural elements and the painted decorative patterns (Wikander, 1986; Winter, 1993). Its main component was the so-called "Geloan" *sima*, which was placed both on the long sides of the roof (lateral *sima*) and on all the three sides of the gable (raking and horizontal *sima*). This *sima* was formed by an upper part with a cavetto profile (always decorated with a painted leaf-pattern) and a roll and a lower fascia, provided with tubular waterspouts on the long sides of the temple. The second component of the "Sicilian system" was the *geison* revetment plaque, usually decorated with a painted guilloche-

pattern. Disc and palmette acroteria, or fine acroterial statues (mostly horsemen, sphinxes and other winged figures), usually located on the ridgepole and at the corners of the roof, enriched and completed the decoration of the Sicilian temples (Danner, 1997).

As mentioned above, the archaeological excavations at Gela have brought to light numerous fragments of architectural terracottas, the most significant of which come from the acropolis area of Molino a Vento and from the dumps of Giardino Calì and Madonna dell'Alemanna. Many scholars have published several of these findings (Bernabò Brea and Carta, 1949-1951; Adamesteanu, 1953, 1956b, 1958; Adamesteanu and Orlandini, 1956, 1960, 1962; Orlandini, 1954, 1956, 1958; Castoldi, 1998; De Miro and Fiorentini, 1976-1977; Ferrara, 2009; Greco, 2009). However, so far they have not gone beyond the traditional methodological approach, only based on the morpho-typological and stylistic classification of the artifacts, and they have not verified the assignment of the products to Geloan artisans. Indeed, contrary to the researches performed, for example, on the Etruscan and center-Italic architectural decorations (Lulof 1996; Rescigno and Sampaolo, 2005), no archaeometric investigations have been carried out on the terracottas from Gela. The unique example available in literature is represented by the study performed on few specimens from the Treasury of Gela at Olympia (Lang and Mommsen, 2006).

Therefore, our research aims to fill this gap by investigating the provenance, the sources of supply of raw materials and the manufacturing technology of this remarkable class of artifacts through a multi-methodological archaeometric approach.

For this purpose, a group of *sima*, *geison* and acroteria fragments, found at Gela and deposited in the local Archaeological Museum, has been examined. The specimens, datable in the 6th century B.C., come from two important archaic sanctuaries areas, namely from the dump context found in 1957 in the Giardino Calì area, in the western part of the acropolis (Orlandini, 1968), and from the dump context excavated in 1951 on the hill of Madonna dell'Alemanna, to the north of the Greek city (Adamesteanu, 1956b) (Figure 1).

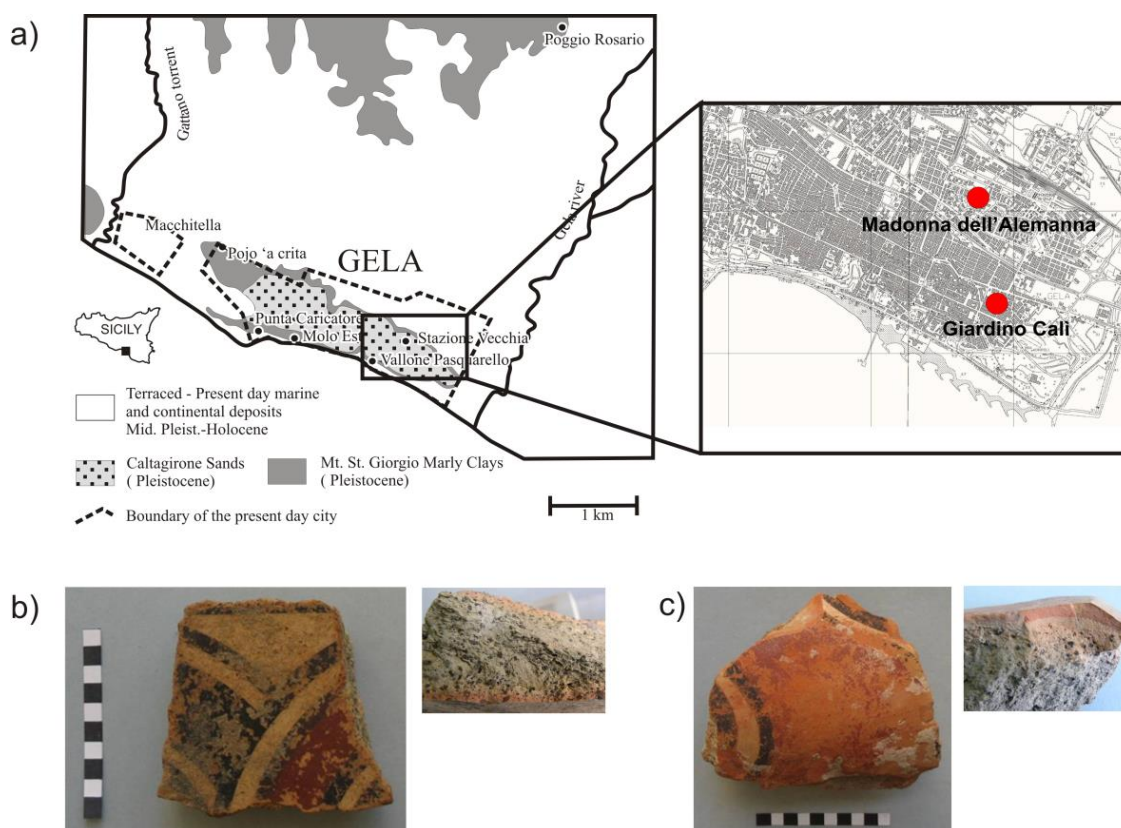


Figure 1. Geographical localization of Giardino Calì and Madonna dell'Alemanna in the city of Gela and geological setting of the area (from Barone et al., 2012). Pictures of (b) geison fragment (GETCA 3) and (c) acroterion fragment (GETCA 10), as examples of the analyzed specimens with painted decoration.

## 2. EXPERIMENTAL

### 2.1 Materials

Twenty samples of fine architectural terracottas have been analyzed: fourteen specimens from the dump of the Giardino Calì area (labeled as GETCA 1-14), and six specimens from the dump of Madonna dell'Alemanna (labeled as MDA 1-6) (Table 1). The samples mainly include "Sicilian" roof friezes, namely geison revetment plaques and "Geloan" sima, as well as a sima of "a mantello" type and three fragments of acroterial statues. On the surface, almost all the samples from Giardino Calì site retain traces of the painted decoration.

As regards the morphology of the profile and the decorative patterns, the sima and geison specimens are more or less comparable with the already published friezes from the sanctuary of the acropolis of Molino a Vento (Bernabò Brea, 1949-1951; Greco, 2009). The only exception are GETCA 1-5 and 11-13 samples from Giardino Calì, which belong to a geison revetment of unknown type, probably related to a larger and maybe older temple. The ceramic paste of all the samples from the Giardino Calì shows homogeneous features, with numerous coarse and medium grained inclusions (1-1.5 mm). The ceramic

paste does not have a homogeneous color, because of the considerable thickness of the wall of the specimens. In detail, the color mainly ranges from reddish yellow (Munsell 5YR 6/6 - 7/6; 7.5YR 7/6) or red (Munsell 2.5YR 5/8 - 6/6 - 6/8) near the surface, and from pale yellow (Munsell 2.5Y 6/6 - 7/4; 5Y 6/3 - 7/3 - 7/4) or gray (Munsell 10YR 5/1) in the inner core. Except the above-mentioned larger geison revetment, the other samples show some traces of a very thin depurated clay slip of slightly lighter color. The acroterial statues fragments (GETCA 9, 10 and 14) have the same coarse clay paste of the friezes, but their surface is always covered by a thick highly depurated clay slip, which was useful to model the figures.

Regarding the typological and decorative appearance, the samples from the Madonna dell'Alemanna area are quite similar to those from the Giardino Calì area (and to those from Molino a Vento), even if different technical features can be recognized. In fact, in order to have a sampling set as comprehensive as possible of the artifacts used in the temples of the city of Gela during the archaic period.

**Table 1.** Macroscopic features of the studied architectural terracottas along with information on samples: ID, inventory number, typological classification and color of clay paste based on the Munsell Soil Color Charts (MI: Munsell index, Munsell, 2000).

Site	Sample ID	Inventory number	Type	Macroscopic features
Giardino Calì	GETCA 1	2647	<i>geison</i>	Compact clay paste with coarse and medium grained volcanic inclusions. Core: 5YR 6/6 (reddish yellow). Surface: 2.5YR 6/8 (light red)
	GETCA 2	2668	<i>geison</i>	Compact clay paste with coarse and medium grained volcanic inclusions. Core: 5YR 7/6 (reddish yellow). Surface: 2.5YR 6/8 (light red).
	GETCA 3	2530	<i>geison</i>	Compact clay paste with coarse and medium grained volcanic inclusions. Core: 5Y 7/3 (pale yellow). Surface: 5YR 7/6 (reddish yellow).
	GETCA 4	2539	<i>geison</i>	Compact clay paste with coarse and medium grained volcanic inclusions. Core: 5Y 7/4 (pale yellow). Surface: 7.5YR 7/6 (reddish yellow). Painted decoration (black).
	GETCA 5	2464	<i>geison</i>	Compact clay paste with coarse and medium grained volcanic inclusions. Core: 5Y 7/4 (pale yellow). Surface: 10YR 7/3 (very pale brown).
	GETCA 6	2098	<i>"Geloan" sima</i>	Compact clay paste with coarse and medium grained volcanic inclusions. Core: 2.5YR 6/6 (light red). Surface: 2.5YR 6/8 (red). Painted decoration (black).
	GETCA 7	2377	<i>"Geloan" sima</i>	Compact clay paste with coarse and medium grained volcanic inclusions. Core: 5Y 6/3 (pale olive). Surface: 5YR 7/8 (reddish yellow). Painted decoration (black).
	GETCA 8	2758	<i>sima of "a mantello" type</i>	Compact clay paste with coarse and medium grained volcanic inclusions. Core and surface: 5YR 6/6 (reddish yellow).
	GETCA 9	2879	<i>acroterion</i>	Compact clay paste, with coarse and medium grained volcanic inclusions. Core and surface: 5Y 6/4 (light reddish brown). Painted decoration (black).
	GETCA 10	2802	<i>acroterion</i>	Compact clay paste, with coarse and medium grained volcanic inclusions. Core: 10YR 5/1 (gray). Surface: 5YR 6/6 (reddish yellow). Highly depurated clay slip. Painted decoration (black and red).
	GETCA11	/	<i>geison</i>	Compact clay paste with coarse and medium grained volcanic inclusions. Core: 5Y 7/3 (pale yellow). Surface: 5YR 7/6 (reddish yellow). Painted decoration (black and creamy white).
	GETCA12	/	<i>geison</i>	Painted decoration (red).
	GETCA13	/	<i>geison</i>	Compact clay paste with coarse and medium grained volcanic inclusions. Core and surface: 2.5Y 6/6 (olive yellow). Painted decoration (black).
	GETCA14	/	<i>acroterion</i>	Compact clay paste with coarse and medium grained volcanic inclusions. Core and surface: 2.5Y 7/4 (pale yellow). Painted decoration (black, red and creamy white).
Madonna dell'Alemanna	MDA1	/	<i>"Geloan" sima</i>	Compact clay paste with small and medium grained white inclusions. Core and surface: 7.5YR 7/4 (pink).
	MDA2	/	<i>geison</i>	Compact clay paste with small and medium grained white inclusions. Core: 10YR 6/1 (gray). Surface: 7.5YR 7/6 (reddish yellow).
	MDA3	/	<i>geison</i>	Compact clay paste with small and medium grained white inclusions. Core: 5Y 7/4 (pale yellow). Surface: 7.5YR 7/6 (reddish yellow)
	MDA4	/	<i>geison</i>	Compact clay paste with small and medium grained white inclusions. Core and surface: 7.5YR 7/6 (reddish yellow).
	MDA5	/	<i>geison</i>	Compact clay paste with small and medium grained white inclusions. Core: 10YR 5/1 (gray). Surface: 7.5YR 7/6 (reddish yellow).
	MDA6	/	<i>"Geloan" sima</i>	Compact clay paste with small and medium grained white inclusions. Core: 2.5Y 7/4 (pale yellow). Surface: 7.5YR 7/6 (reddish yellow).

Among the architectural terracottas from Madonna dell'Alemanna we have intentionally chosen the only specimens with a clay paste much more depurated and compact than the others, and without coarse inclusions. This technical peculiarity is probably due to the different size of the roof revetments; in fact, the selected fragments have a thinner wall than the other terracottas, likely belonging to smaller friezes, namely to minor sacred buildings.

The surface of almost all samples from Giardino Calì dumps is painted with the typical archaic colors, i.e. black, red and creamy white, which have been analyzed in order to investigate the composition of the pigments and the firing technique. According to the macroscopic examination, the three colors appear directly applied on the ceramic surfaces, without any base slip (similar to that documented, for example, on the painted antefixes from Gela: see Castoldi, 1998). In some cases, there are traces of engraved preparatory drawings (Winter, 1993).

## 2.2 Methods

Petrographic (OM), mineralogical (XRD), chemical (XRF and SEM-EDS) and spectroscopic ( $\mu$ -Raman spectroscopy) analyses have been performed on the studied samples.

In order to characterize the artifacts in terms of texture, groundmass and inclusions, a selection of representative samples have been analyzed in thin section by optical microscopy, using a polarized transmitted light microscope Nikon Eclipse E400 POL. The mineralogical composition of specimens has been determined by means of X-ray diffraction using a Siemens D5000 instrument, with Cu K $\alpha$  radiation, 40 kV, 30 mA and Ni filter. Randomly oriented powders have been scanned from 2° to 45° 2 $\theta$ , with a 0.02° 2 $\theta$  step size and a counting time of 3 s per step. Chemical data have been obtained by means X-ray fluorescence (XRF) spectrometry (PHILIPS PW 2404/00) on powder-pressed pellets; total loss on ignition (LOI) was gravimetrically estimated after overnight heating at 950 °C. Chemical data were treated with the statistical methodology mainly based on the log-ratio technique introduced by Aitchison (Aitchison, 1986) and employed in order to avoid the constant sum problem. The centred log-ratio transformation (clr) of data is applied as follows:  $x \in \text{SD} \rightarrow y = \ln(xD / gD(x)) \in \text{RD}$ , where  $x$  is the vector of the  $D$  elemental compositions,  $y$  is the vector of the log-transformed compositions,  $xD = (x_1, x_2, \dots, x_D)$  and  $gD(x) = (x_1 \cdot x_2 \cdot \dots \cdot x_D)^{1/D}$ . This operation transforms the raw data from their constrained sample space, the simplex  $S_d(d = D - 1)$ , into the real space  $R_d$ , in which parametric statistical methods can be applied to the transformed data. Subsequently, the clr-transformed data set was ex-

plored by biplots, a graphical representation of variables and cases projected on to principal component planes. Both the clr-transformation and the biplot calculations were obtained by using CoDaPack (Thió-Henestrosa and Martín-Fernández, 2011), a compositional software that implements the basic methods of analysis of compositional data based on log-ratios.

Additionally, scanning electron microscopy (SEM-EDS) measurements have been performed in order to investigate chemical composition of the volcanic inclusions of some analyzed samples. Data have been collected using a Tescan Vega LMU scanning electron microscope, equipped with an EDAX NeptuneXM4-60 micro-analyzer, characterized by an ultra-thin Be. Measurements have been carried out by using spot mode analysis on polished thin sections, with 20 kV accelerating voltage and 0.2 nA beam current.

Finally, the painted decorations have been investigated through chemical (SEM-EDS) and spectroscopic analyses, in order to obtain information on colors composition and technological features. In particular, micro-Raman spectra have been acquired with a Raman Jasco NRS-3100 apparatus, equipped with a microscope with x10, x20 and x100 objectives, by using a laser excitation source at 785 nm; laser power has been controlled by means of a series of density filters, in order to avoid heating effects. Depth resolution was set to few micrometers by means of a confocal hole. The system has been calibrated using the 520.7 cm<sup>-1</sup> Raman band of silicon before each experimental session.

## 3. RESULTS

### 3.1 Mineropetrographic analyses

Petrographic analyses on thin section have been performed on a representative selection of studied samples with the aim at characterizing texture and mineralogical composition, following the scheme proposed by Whitbread (1995). Three different fabrics have been recognized (Figure 2), mainly characterized by fossil-rich and micaceous groundmass, with and without volcanic inclusions.

In detail, Fabric A (specimens GETCA2 and GETCA8; Figure 2.a) is characterized by fossil-rich groundmass and volcanic inclusions. The vuggy microstructure is due to single-double space distributed vugs and vesicles, the latter one partially preferred oriented (in GETCA8). The groundmass is quite homogeneous and fossil-rich, with scarce micas in GETCA8. The color is mainly brownish and the optical activity is from medium (GETCA2) to low (GETCA8). The inclusions (c:f = 40:60) are mainly represented by coarse-grained and polymodal vol-



canic rock fragments and by quartz, plagioclase and pyroxene. Amorphous phases are also present, red in color and with altered edges.

Fabric B (specimens GETCA4 and GETCA7; Figure 2.b) is characterized by a more heterogeneous micaceous groundmass and volcanic inclusions. The vuggy microstructure exhibits open spaced vugs and vesicles, the latter one preferential oriented. The groundmass, from yellowish to yellow-brownish in color, is very heterogeneous; therefore, it is probably the result of the mixture of two different clay sediments (micas-rich and mica-poor). It also exhibits low/medium-low optical activity. Inclusions (c:f = 30:70) are characterized by coarse grain sized volcanic rock fragments, and minor amount of quartz, plagioclase pyroxene and altered feldspars. Amorphous phases are present, both red and black, mainly characterized by evident altered edges.

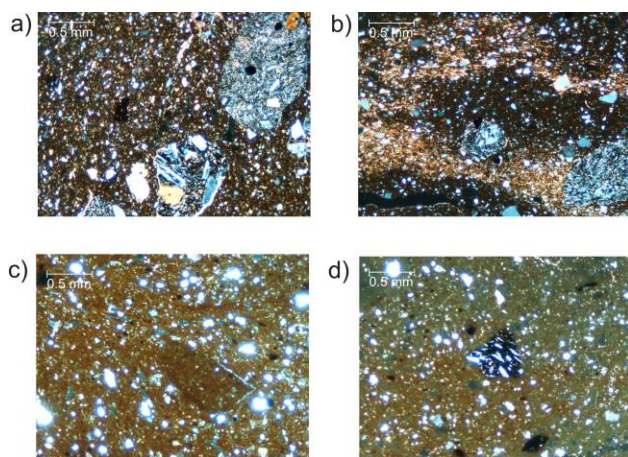


Figure 2. Microphotographs of samples representative of the petrographic fabrics recognized by thin section analysis: (a) GETCA 8, (b) GETCA 7, (c) MDA 5, and (d) MDA 3.

Finally, Fabric C (specimens MDA1-MDA6; Figure 2.c-d) is characterized by fossil-rich and micaceous groundmass with chamotte inclusions. The vuggy microstructure is due to (in order of abundance) channel, vugs, vesicles, mainly open spaced; preferred oriented vesicles can be observed in samples MDA1 and MDA2. The groundmass is mainly from brown-yellowish to brown-reddish in color and

exhibits a medium-low optical activity, high only in MDA5. It is also homogeneous, with fine quartz and mica (scarce in MDA6) and microfossil molds, with re-crystallized calcite. Inclusions (c:f = 10:90), sub-angular in shape and mainly exhibiting a bimodal grain size distribution (unimodal in MDA4, MDA, MDA6), are characterized by dominant fine-grained chamotte (scarce in MDA2), quartz, plagioclase and rare metamorphic quartz in MDA5. Amorphous phases are also present, mainly reddish-black in color. Noteworthy is that the sample MDA3 exhibits the same textural features of the other MDA specimens, except for the presence of volcanic inclusions (small fragment of volcanic rocks, glass, plagioclase and pyroxene).

In order to obtain information on firing temperature, for the evaluation of which the groundmass optical activity can be also used as supporting data, semi-quantitative mineralogical analyses have been carried out by means X-ray diffraction method. In fact, as it is well known (Cultrone et al., 2011; Maggetti, 1982; Riccardi et al., 1999), the presence of specific mineralogical phases in archaeological ceramics are suitable to esteem firing temperature.

In particular, in Ca-rich clays, chemical reactions between minerals in the clay allow the newly formation of Ca-silicates phases as gehlenite, anorthite and diopside, indicative of high firing temperature (about 850-900 °C); of course, neither anorthite nor diopside can be used for temperature esteem when related to tempers composition. In the case of poor-Ca clays, the absence of carbonates does not allow the formation of Ca-silicate and changes are mainly related to textural features, with the only transformation of low-T phases in high T-phases; however, some minerals can be used as temperature indicators, as phyllosilicates and hematite (Cultrone et al., 2001). In fact, in XRD patterns of Ca-poor clay materials, a gradually reduction of peaks intensity of phyllosilicate due to dehydroxilation of clay minerals and an increase of peaks related to hematite can be observed with the increasing of firing temperature.

Table 2. Mineralogical data of the studied samples. For GETCA samples, the semi-quantitative XRD results are reported for both total bulk and only groundmass. Qtz = Quartz; CM = clay minerals; Cal = calcite; Ab = albite; An = anorthite; Di = diopside; Hem = Hematite; Pl = plagioclase; Gh = gehlenite; Ms = muscovite. The number of (+) is related to the mineralogical phase abundance; tr = trace.

Sample ID	Bulk/groundmass	Qtz	Cal	An	Ab	Di	Hem	Gh	CM	Ms
GETCA1	Total bulk	+++		++	+	+	+	tr	tr	
GETCA1	groundmass	+++	tr	tr		tr	++	++	tr	
GETCA2	Total bulk	+++		++		+				+
GETCA2	groundmass	+++	tr-	tr		tr		tr		
GETCA3	Total bulk	+++		++		+	tr	tr	tr	
GETCA3	groundmass	+++	tr	tr		tr	+	+	+	
GETCA4	Total bulk	+++		++		+				+
GETCA4	groundmass	+++	tr	tr	++	tr	+	tr		

GETCA5	Total bulk	+++		++		+	tr	tr	tr	
GETCA5	groundmass	+++	tr	tr		tr	+	+	tr	
GETCA6	Total bulk	+++		++		+	tr	+	tr	
GETCA6	groundmass	+++	tr	tr		tr	+	+	tr	
GETCA7	Total bulk	+++		++		++	tr	tr		
GETCA7	groundmass	+++	tr	tr		tr	+	+	tr	
GETCA8	Total bulk	+++		+	+					
GETCA8	groundmass	+++	tr	tr		tr	+	tr	tr	
GETCA9	Total bulk	+++	tr	++		++	+	tr	tr	
GETCA9	groundmass	+++	tr	+		+	+	tr	tr	
GETCA10	Total bulk	+++	tr	++		+	tr	tr	tr	
GETCA10	groundmass	+++	tr	+		tr	+	tr	tr	
MDA 1	Total bulk	+++	++	+		+	+	tr	+	
MDA 2	Total bulk	+++	++	+		+	+		+	
MDA 3	Total bulk	+++	tr	++		++	+	+	+	
MDA 4	Total bulk	+++	tr	++		+	+	+	+	
MDA 5	Total bulk	+++	tr	+		+	+		+	
MDA 6	Total bulk	+++	++	++		++	+	+	+	

In consideration of the presence of volcanic rock fragments, and plagioclase and pyroxene as inclusions, in samples labeled as GETCA, XRD analyses have been carried out on both total bulk and on the only groundmass, the latter one obtained by gently crushing samples in agate mortars and separating magnetically the volcanic inclusions. The semi-quantitative data obtained by the analysis of X-ray patterns are reported in Table 2. On the basis of the obtained data and the information gained from the optical activity features of analyzed materials, it is possible to assess an overall medium-high firing temperature for both the set of studied architectural terracottas (namely GETCA and MDA).

In detail, in GETCA samples, the analysis of XRD patterns related to the only groundmass allows to highlight the presence of newly formed minerals as anorthite, diopside and gehlenite, that suggest a firing temperature of about 850-950 °C, according to the medium-low optical activity observed in thin sections. Similar mineralogical composition has been obtained for samples labeled as MDA, in which the presence of hematite, anorthite, and diopside can be considered indicators of medium-high firing tem-

peratures (850-950 °C, in accordance with the medium-low groundmass birefringence). Exception is represented by sample MDA3, in which the presence of volcanic inclusions does not allow to esteem firing temperatures because of its mineralogical composition. Finally, noteworthy is that, in some cases, the coexistence of newly formed minerals and calcite has been observed, especially in samples characterized by fossil-rich groundmass; this aspect can be explained only considering the presence of secondary calcite due to circulation of Ca-rich solutions in burial conditions (Cultrone et al., 2014).

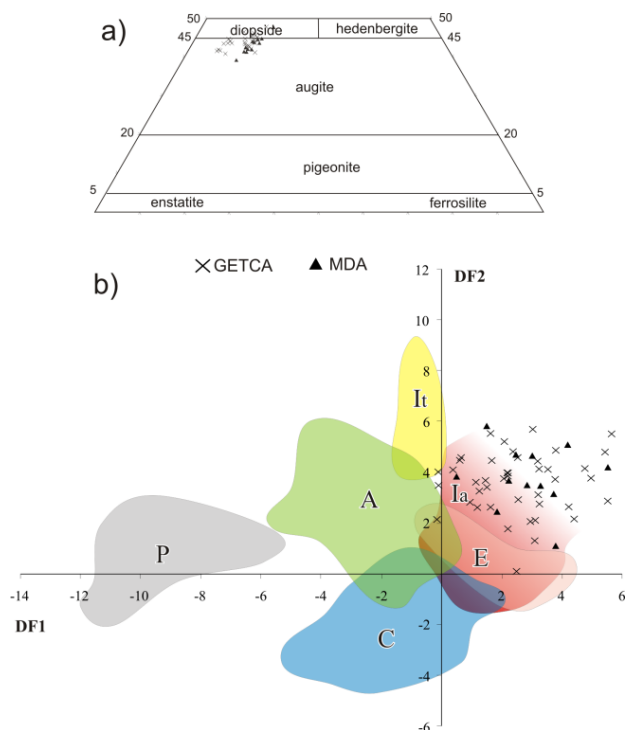
### 3.2 Chemical analysis on pyroxenes

According to Barone et al. (2010), the petrochemical characterization of the volcanic inclusions may allow obtaining useful information on the provenance of archeological artifacts in terms of sources of supply of raw materials. In particular, as clinopyroxenes keep the original composition unaltered, their chemical composition can unambiguously discriminate volcanic products belonging to distinct magmatic provinces.

Table 3. Average compositions and relative standard deviations of pyroxenes from each analysed sample.

Oxide wt%	GETCA 4 (n = 14)		GETCA 2 (n = 16)		GETCA 7 (n = 13)		GETCA 8 (n = 3)		MDA 3 (n = 2)	
	Mean	St. Dev.	Mean	St. Dev.	Mean	St. Dev.	Mean	St. Dev.	Mean	St. Dev.
SiO <sub>2</sub>	51.01	1.36	50.59	1.44	51.67	1.58	50.81	0.72	50.27	1.45
TiO <sub>2</sub>	1.19	0.49	1.15	0.41	0.93	0.52	1.25	0.16	1.37	0.36
Al <sub>2</sub> O <sub>3</sub>	3.65	0.93	4.21	1.38	3.30	1.36	4.19	1.03	4.73	1.02
Cr <sub>2</sub> O <sub>3</sub>	0.18	0.10	0.39	0.45	0.40	0.36	0.12	0.02	0.14	0.11
FeO	7.96	1.12	6.86	1.60	5.95	1.73	7.00	0.45	7.98	0.70
MnO	0.31	0.08	0.25	0.10	0.26	0.09	0.25	0.10	0.27	0.10
MgO	14.97	1.07	15.04	1.41	16.03	1.68	15.10	0.24	14.46	1.03
CaO	19.94	0.61	20.26	2.58	20.90	0.51	20.57	0.45	20.00	1.15
Na <sub>2</sub> O	0.60	0.11	0.49	0.14	0.44	0.14	0.54	0.01	0.65	0.08
K <sub>2</sub> O	0.20	0.14	0.13	0.04	0.14	0.06	0.16	0.04	0.13	0.04

On the basis of the aforementioned, from the studied architectural terracottas exhibiting volcanic inclusions (Fabric A and B, as well as sample MDA3, belonging to Fabric C), 48 pyroxenes have been selected and analyzed; the average compositions are listed in Table 3.



**Figure 3.** (a) Classification diagrams (Morimoto et al., 1988) of pyroxenes from volcanic inclusions in GETCA and MDA3 samples, and (b) DF1 vs. DF2 diagram showing the correspondence between clinopyroxenes from volcanic rocks and those from terracottas samples. It = Hyblean tholeiites; Ia = Hyblean alkaline basalts; E = Mt. Etna; A = Aeolian Arc; P = Pantelleria Island; C = Campanian province.

The preliminary classification of the analyzed pyroxenes has been made according to Morimoto et al. (1988); the obtained results (Figure 3.a) allow to highlight a quite homogeneous sub-calcic compositions; in fact, the analyzed pyroxenes mainly fall in fields from diopside to augite. The statistical analysis of pyroxenes obtained by plotting chemical data on the DF1 vs. DF2 diagram proposed by Barone et al. (2010) (Figure 3.b), in which the different populations of southern-Italy and Sicilian volcanic products are clustered into clearly distinguishable groups, shows that the inclusions identified in the Geloan architectural terracottas have a strong affinity with the products of southeast Sicilian magmatic provinces (Iblean alkaline basalts and Mt. Etna products, small overlapped in the pyroxenes discrimination diagram). Therefore, this result suggests these areas as possible source of supply of the raw materials employed in the Geloan revetments manufacture.

### 3.3 Geochemical data

Ceramic materials are usually characterized by two main components: the plastic fraction, consisting in the clay sediments employed in the manufacture of the artifacts, and the aplastic one, due to aggregates, that can be included in the original sediment or even intentionally added by artisans to the mixture for technical aims. From the chemical point of view, the composition of the whole ceramic artifact is therefore the sum of the geochemical features of both clays and inclusions. In this perspective, in order to investigate aspects as the provenance of the artifacts, the contribute of possible intentionally added inclusions in changing the geochemical compositions of clays has to be considered. Therefore, on the basis of the above mentioned, in this study, chemical analysis by XRF have been performed on the only groundmass of the samples with the aim at obtaining the chemical composition of the solely clay sediments and integrating these data with the provenance information gained from the chemical analysis of pyroxenes in volcanic inclusions. Only in this way, the possibly common or different geographical source of both plastic fraction and aggregates can be verified.

The chemical composition of terracottas samples obtained by XRF on the groundmass fraction is reported in Table 4. The results suggest a quite homogeneous composition for the overall studied samples; however, some differences in term of major and trace element abundances between the two sets of architectural terracottas (namely GETCA from Giardino Cali and MDA from Madonna dell'Alemanna) can be inferred. In particular, GETCA samples exhibit higher contents of  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$  and Co than MDA ones; on the contrary, these latter ones are characterized by higher levels of Ni.

The statistical treatment of data allows better highlighting the differences in geochemical features between the two sets of materials, as well as obtaining additionally information on the provenance of the clayey sediments.

In fact, data have been compared with reference groups consisting in several ceramics and clayey raw materials of certain Geloan provenance (Aquilina et al., 2012; Barone et al., 2012), and with ceramics and clays from Siracusa (Barone et al., 2014) and Lentini (Barone et al., 2005). The selection criterion of the reference groups used to compare the terracottas is based on the similarity between petrographic features of studied materials and other Sicilian archaic artifacts, as well as on the results obtained from chemical analysis of pyroxenes, indicating the Iblean magmatic province as source of the volcanic aggregates.



**Table 4.** Chemical composition of the analyzed samples. Major element are reported in wt%, minor elements in ppm.

Sample ID	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>
GETCA1	57.89	0.96	15.09	6.93	0.09	2.11	12.55	1.57	2.32	0.49
GETCA2	58.31	0.98	14.97	7.26	0.09	2.20	11.69	1.71	2.22	0.56
GETCA3	57.19	0.95	14.93	6.77	0.09	2.39	13.59	1.61	2.09	0.39
GETCA4	57.36	0.95	14.69	6.74	0.09	2.35	13.73	1.64	2.11	0.35
GETCA5	58.34	0.87	14.03	6.26	0.08	2.37	14.29	1.61	1.83	0.31
GETCA6	58.53	0.92	14.06	6.65	0.09	2.15	13.50	1.42	2.34	0.33
GETCA7	58.65	0.84	14.17	6.33	0.08	2.22	13.89	1.25	2.23	0.34
GETCA8	59.69	0.90	14.38	6.17	0.08	1.85	12.73	1.37	2.51	0.30
GETCA9	61.08	0.72	13.84	5.57	0.08	2.11	13.45	0.94	1.99	0.22
GETCA10	59.56	0.90	14.63	6.47	0.08	2.03	12.18	1.48	2.31	0.35
MDA1	62.80	0.81	12.91	5.32	0.11	2.29	12.27	0.79	2.37	0.33
MDA2	61.72	0.86	12.94	5.58	0.10	2.31	12.97	0.80	2.53	0.18
MDA3	61.06	0.89	13.56	5.68	0.07	2.72	12.80	1.10	1.96	0.16
MDA4	60.67	0.92	13.66	5.70	0.10	2.75	12.43	0.92	2.61	0.26
MDA5	62.82	0.86	13.05	5.13	0.08	2.39	12.04	0.91	2.56	0.16
MDA6	62.90	0.80	12.36	4.99	0.08	2.96	13.11	1.03	1.62	0.16

Sample ID	Sr	V	Cr	Co	Ni	Zn	Rb	Y	Zr	Nb	Ba	La	Ce	Pb	Th
GETCA1	632	80	71	24	28	53	65	28	232	29	475	44	86	16	7
GETCA2	444	80	66	23	34	51	44	12	149	11	454	48	97	13	6
GETCA3	615	82	67	25	29	53	59	26	226	30	419	47	118	15	7
GETCA4	604	79	67	27	31	59	56	26	225	29	436	45	94	14	9
GETCA5	668	75	70	23	31	53	49	27	228	24	368	38	92	11	6
GETCA6	588	78	62	24	32	57	63	27	226	26	421	38	78	15	9
GETCA7	559	73	70	23	31	52	67	28	236	24	344	40	91	19	8
GETCA8	579	82	66	25	30	49	60	27	219	23	355	33	83	14	7
GETCA9	222	65	79	18	43	46	33	6	101	n.d.	264	30	77	3	n.d.
GETCA10	598	80	63	25	28	49	64	28	230	24	423	35	88	17	8
MDA1	677	94	88	14	37	91	72	24	270	16	659	44	66	18	9
MDA2	603	100	90	11	42	87	84	24	227	17	378	31	74	18	9
MDA3	436	104	89	7	49	71	40	27	161	6	341	35	65	0	8
MDA4	495	93	92	8	50	72	50	30	144	3	592	46	86	17	8
MDA5	348	91	76	6	47	64	35	15	105	1	373	38	71	12	6
MDA6	354	76	66	4	43	56	20	18	146	2	377	28	57	13	6

The biplot of Figure 4 shows a good accordance between GETCA and MDA samples, and the Geloan ceramics and clays. In the case of samples exhibiting volcanic inclusions from the southeast Sicilian magmatic provinces, the results clearly neglect the expectations, as they also group with Geloan reference materials. This result suggests an overall local production of the analyzed specimens, claiming a different provenance of clays and aggregates used in the manufacture of GETCA terracottas.

### 3.4 Painted decoration characterization

The analytical characterization of the painted decoration, representative of the different colors observed on GETCA samples (see Table 1), have been obtained by performing both chemical and spectroscopic analyses. In detail, SEM-EDS measurements, performed by using spot mode analysis on small chips drawn from the painted surfaces, have allowed obtaining quantitative data about the chemical composition of the pigmenting agents along with eventual components related to deterioration processes. The average

chemical composition of the analyzed samples, expressed as weight percentage (wt%), is reported in Table 5. Regarding black surfaces, the color is due to the presence of manganese oxide; on creamy white surfaces, silica, calcium and alumina (in order of abundance) have been detected; finally, red surfaces are characterized by iron oxides. It is worth of note that on some surfaces (for example on the GETCA7 sample), chloride and sulfate have been also detected, interpretable as deterioration products.

In order to obtain in-depth information on pigments, micro-Raman non-destructive and non-invasive analyses have been carried out on the painted surfaces. The analysis of Raman spectra (Figure 5.a) have allowed to identify pyrolusite (strong band at about  $640\text{ cm}^{-1}$  ascribed to Mn-O stretching mode; Sepúlveda et al., 2015), meta-kaolin (Frost, 1997) and haematite (226, 292, 410, 496,  $611\text{ cm}^{-1}$ ; Zoppi et al., 2008) as pigments for black, creamy white and red, respectively.

As regards the firing behavior, taking as reference the assumptions recently made in a multidisciplinary study on some archaic architectural terracottas from Capua (Rescigno and Sampaolo, 2005), we have also verified the possibility that the Gelan artisans have performed one or more firing phases to obtain the different colors. In fact, according to that study, the artifacts from Capua would have been fired twice (the first time at high temperature, with diluted base colors; the second time at a lower tempera-

ture, with the complete polychrome decoration), or, more probably, in a single firing cycle, but with a skillful alternation of oxidizing and reducing atmosphere in order to achieve the colors red and black from pigments consisting of iron oxides.

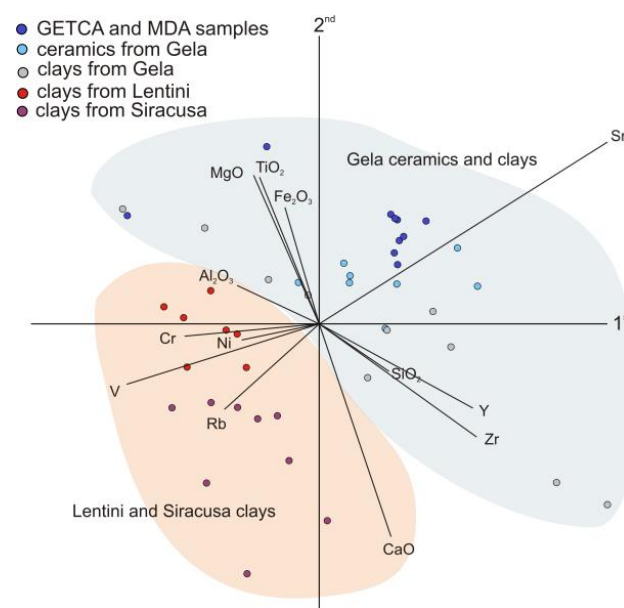


Figure 4. Biplot of the two principal components.

Table 5. Semi-quantitative average chemical composition (wt%) of pigment layers (black, red and creamy white) in studied samples obtained by EDS analyses.

	Black layers				Red layers		Creamy layers
	GETCA4	GETCA 7	GETCA 11	GETCA 13	GETCA 12	GETCA 14	GETCA 11
Na <sub>2</sub> O	0.8			0.5±0.3	0.5±0.3	0.4	
MgO	2.0±0.5	2.2±0.8	2.7±0.4	3.6±0.5	1.0±0.2	2.7±0.8	5.7±4.0
Al <sub>2</sub> O <sub>3</sub>	7.8±1.0	7.3±2.0	8.3±0.6	12.2±3.6	8.7±2.5	9.4±1.1	<b>10.1±4.9</b>
SiO <sub>2</sub>	17.9±4.7	29.4±8.5	29.5±3.8	29.8±14.6	23.9±2.6	31.0±7.3	<b>58.7±12.6</b>
SO <sub>3</sub>		14.1±5.7					
Cl <sub>2</sub> O		0.8±0.1					
K <sub>2</sub> O	0.9±0.1	1.0±0.6			1.6±0.8	0.5±0.2	2.0±1.1
CaO	4.6±1.5	21.7±6.0	11.6±4.3	5.3±1.2	3.6±2.1	10.9±0.4	<b>15.5±6.1</b>
TiO <sub>2</sub>	0.7±0.4	0.5±0.2				0.5±0.1	1.1±0.2
MnO	<b>24.4±3.3</b>	<b>7.0±0.2</b>	<b>15.3±2.0</b>	<b>16.3±3.0</b>			
FeO	41.0±4.4	18.7±2.0	32.7±5.5	32.4±9.7	<b>60.6±7.9</b>	<b>44.5±6.9</b>	6.9±4.4

Effectively, according to the macroscopic observation, there are no traces of any diluted base color in our samples and the creamy white color looks applied in the decorative patterns as well as the other two colors, which means that the artisans have not used it as a slip. Therefore, for Gela specimens we

can exclude the hypothesis of two different firing phases.

Moreover, the detection of Mn-based pigment in black color suggests very interesting implications in this regard. In fact, contrary to the use of iron oxides, which during firing needs two different atmosphere

conditions (oxidizing and reducing, respectively) in order to produce the colors red and deep black, the use of manganese oxides allows to obtain stable black hue also in an oxidizing atmosphere and with firing temperature about 950 °C. Therefore, by employing this technical device, a single firing phase in oxidizing atmosphere was just enough to obtain both colors.

A confirmation of the proposed hypothesis - in this case, however, regarding the creamy white color - comes from an experimental study, which we have conducted on laboratory tests samples, slipped with depurated kaolin and fired in controlled oxidizing conditions at 750, 850 and 950 °C. Taking advantages from both the structural modifications of kaolin-based materials along with temperature and the sensitiveness of Raman spectroscopy to supply structural information on minerals, micro-Raman analyses have been performed on the laboratory test samples and spectra have been compared with data acquired on Geloan terracottas (Figure 5.b).

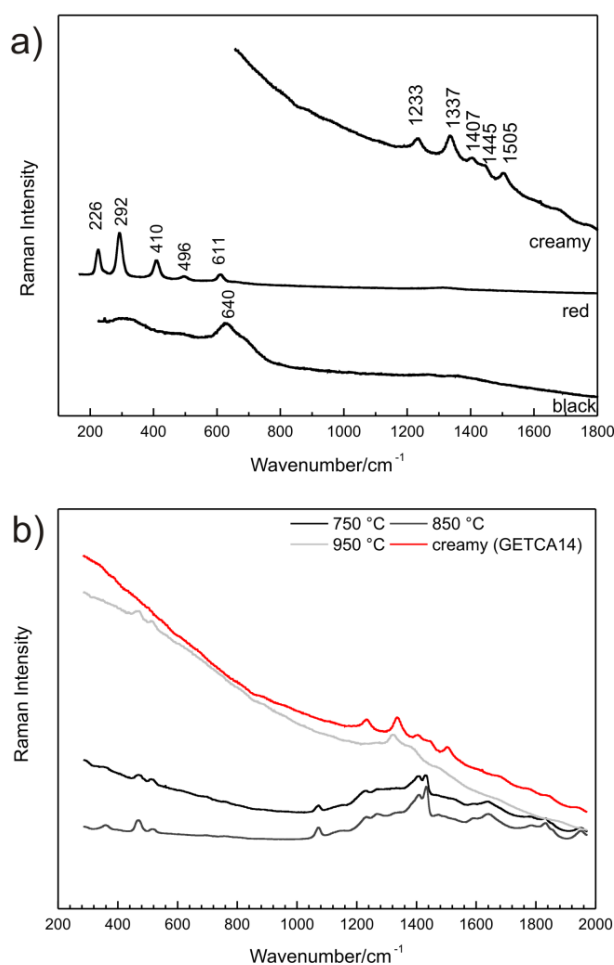


Figure 5.  $\mu$ -Raman spectra collected on (a) black, red and creamy white surfaces, and on (b) laboratory samples slipped with kaolin and fired at different temperatures along with spectra collected on GETCA 14 sample for comparison.

The obtained results suggest a good spectral matching between the creamy white surfaces and the test samples fired at 950 °C. It is of great interest that the temperature esteemed on the basis of spectroscopic data acquired on painted decorations are in agreement with the firing  $T_{\max}$  suggested by the mineralogical composition of the ceramic bulk; in this sense, it can be assumed a single firing phase for the manufacture of both terracotta and decoration.

#### 4. DISCUSSIONS AND CONCLUSIONS

All the analyses performed on the Geloan architectural terracottas have provided very interesting results, filling a gap in the current archaeological and archaeometric literature on this important class of artifacts.

First, according to our investigations, all the studied specimens seem to have been manufactured in Gela, because the petrographic and chemical characteristics of the ceramic bulk show a good agreement with the published data on local raw materials and locally produced ceramics. The slight differences in chemical composition between the two set of samples from Giardino Calì and that from Madonna dell'Alemanna may be due to the use of distinct local sources of clay supply. In all cases, we can assign to Gela this production of high quality architectural decorations, confirming with laboratory data a hypothesis so far only supported by archaeological arguments.

The analyses have also provided significant information concerning the manufacturing technology. In particular, in the samples from Giardino Calì, the petrographic investigations have revealed an abundant presence of intentionally added temper of non-local provenance. The specimens are in fact characterized by coarse-grained volcanic inclusions, which are absent in the clay sources within the territory of Gela (see Figure 1). The chemical analyses performed on the pyroxenes have indicated their strong affinity with the products of southeast Sicilian magmatic provinces (Iblean alkaline basalts and Mt. Etna products). Therefore, we can hypothesize that the Geloan artisans imported the volcanic material from neighbouring areas and added it to the clay paste in order to improve the production process. Indeed, they surely knew that the presence of numerous coarse inclusions reduces the plasticity of clay, thus making the artifacts more resistant during the drying and firing phases and limiting the risk of cracks or deformations. But, why to choose volcanic materials of non-local provenance? Probably because the artisans had experienced that these materials ensured a better performance in the case of large size and painted artifacts of exceptional value, as the architectural terracottas from Giardino Calì. Conversely, in

the case of smaller size or even undecorated roof revetments, it was not necessary to use a very coarse clay paste with a specific added temper, as demonstrated by the results of the analyses on the architectural terracottas from Madonna dell'Alemanna. Indeed, these terracottas, belonging to smaller size revetments, therefore to minor sacred buildings, are characterized by absence of volcanic inclusions.

Regarding the painted decoration, both chemical and spectroscopic analyses have given relevant data on the composition of colors and on the firing behaviour. For red and black colors, the use of iron oxides and pyrolusite, respectively, has been identified, while depurated kaolin has been detected in the creamy white color. The use of manganese oxides in order to obtain the black color, as well as the spectroscopic evidences on the kaolin, strongly suggest a

single firing phase in oxidizing atmosphere at about 900-950 °C for the manufacture of both ceramic bulk and painted decoration.

In conclusion, the archaeometric approach applied to the study of the Geloan architectural terracottas can be considered a starting point for a more comprehensive interpretation of the numerous archaeological issues related to the coroplastic production in Sicily during the archaic age. Thanks to the availability of these new analytical data and the definition of the manufacturing characteristics of the Geloan production, future studies on roof revetments from other Greek colonies in Sicily could be approached in the perspective of providing a detailed overview on the various manufacturing traditions as well as unveiling the local coroplasts "techne".

## REFERENCES

- Adamesteanu, D. (1953) Coppi con testate dipinte a Gela. *Archeologia Classica* V, 1-9.
- Adamesteanu, D. (1954) Uno scarico di fornace ellenistica a Gela. *Archeologia Classica* VI, 129-132.
- Adamesteanu, D. (1956<sup>a</sup>) Via Dalmazia. Scoperta di una fornace greca arcaica. *Notizie degli Scavi* X, 277-281.
- Adamesteanu, D. (1956b) Madonna dell'Alemanna. Scoperta di una nuova area sacra. *Notizie degli Scavi* X, 382-392.
- Adamesteanu, D. (1958) Nuove antefisse dipinte di Gela. *Archeologia Classica* X, 9-13.
- Adamesteanu, D., Orlandini, P. (1956) Gela. Scavi e scoperte 1951-1956. *Notizie degli Scavi* X, 203-401.
- Adamesteanu, D., Orlandini, P. (1960) Gela. Scavi e scoperte 1951-1956. *Notizie degli Scavi* XIV, 67-246.
- Adamesteanu, D., Orlandini, P. (1962) Gela. L'acropoli di Gela. *Notizie degli Scavi* XVI, 340-408.
- Aitchison, J., 1986. *The statistics analysis of compositional data*. Chapman and Hall, London, UK.
- Aquila, E., Barone, G., Mazzoleni, P., Ingoglia, C. (2012) Petrographic and chemical characterisation of fine ware from three Archaic and Hellenistic kilns in Gela, Sicily. *Journal of Cultural Heritage* 13, 442-447.
- Barone, G., Mazzoleni, P., Aquila, E., Barbera, G. (2014) The Hellenistic and roman Syracuse (Sicily) fine pottery production explored by chemical and petrographic analysis. *Archaeometry* 56, 70-87.
- Barone, G., Mazzoleni, P., Spagnolo, G., Aquila, E. (2012) The transport amphorae of Gela: a multidisciplinary study on provenance and technological aspects. *Journal of Archaeological Science* 39, 11-22.
- Barone, G., Lo Giudice, A., Mazzoleni, P., Pezzino, A., Barilaro, D., Crupi, V., Triscari, M. (2005) Chemical characterization and statistical multivariate analysis of ancient pottery from Messina, Catania, Lentini and Siracusa (Sicily). *Archaeometry* 47, 745-762.
- Barone, G., Belfiore, C.M., Mazzoleni, P., Pezzino, A., Viccaro, M. (2010) A volcanic temper based approach for provenance studies of archaeological ceramics from Southern Italy. *Journal of Archaeological Science* 37, 713-726.
- Bernabò Brea, L., Carta, R. (1949-1951) L'Athenaion di Gela e le sue terrecotte architettoniche. *Annuario della Scuola Archeologica Italiana di Atene* XXVII-XXIX, 7-102.
- Castoldi, M. (1998) Le antefisse dipinte di Gela. *Contributo allo studio della pittura siceliota arcaica*, Milano.
- Cultrone, G., Rodriguez-Navarro, C., Sebastian, E., Cazalla, O., De la Torre, M.J. (2001) Carbonate and silicate phase reactions during ceramic firing. *Eur J Mineral.* 13, 621-34.
- Cultrone, G., Molina, E., Arizzi, A. (2014) The combined use of petrographic, chemical and physical techniques to define the technological features of Iberian ceramics from the Canto Tortoso area (Granada, Spain). *Ceramics International* 40, 10803-10816.
- Danner, P. (1997) *Westgriechische Akrotere*, Mainz am Rhein.
- De Miro, E., Fiorentini, G. (1976-1977) Gela: scavi dell'acropoli 1973-1975. *Kokalos* XXII-XXIII, II, 1, 430-447.
- De Miro, E., Fiorentini, G. (1983) Gela protoarcaica. *Annuario della Scuola Archeologica Italiana di Atene* LXI, 53-104.
- Ferrara, B. (2009) Acroteri a Gela alla luce delle nuove acquisizioni. In *Deliciae Fictiles IV*, Lulof, P., Rescigno, C. (Eds.), Oxford, pp. 464-476.

- Frost, R.L. (1997) The structure of the kaolinite minerals - a FT-Raman study. *Clay Minerals* 32, 65-77.
- Greco, G. (2009) Per una revisione delle terrecotte architettoniche di Gela. In *Deliciae Fictiles IV*, Lulof, P., Rescigno, C. (Eds.), Oxford, pp. 446-455.
- Heiden, J. (1995) Die Tondächer von Olympia. *Olympische Forschungen* XXIV.
- Lang, M., Mommsen, H. (2006) Neutronenaktivierungsanalysen zur Herkunftsbestimmung des Daches des Geloer Schatzhauses in Olympia. In *Archäometrie und Denkmalpflege*, Hahn, O., Stege, H. (Eds.) Jahrestagung der Staatlichen Akademie der Bildenden Künste, Stuttgart, pp. 166-168.
- Lulof, S. (1996) The ridge-pole statues from the late archaic temple at Satricum, Amsterdam.
- Munsell, A.H. (2000) Munsell soil color chart. Gretag, Macbeth, New Windsor.
- Maggetti, M. (1982) Phase analysis and its significance for technology and origin. In *Archeological Ceramics*, Olin, J.S., Franklin, A.D. (Eds.), Washington, Smithsonian Inst. Press, pp. 121-33.
- Mallwitz, A. (1972) Olympia und seine Bauten, München.
- Mertens-Horn, M. (1990) Archaische Tondächer Westgriechischer Typologie in Delphi und Olympia. *Hesperia* 59, 235-248.
- Morimoto, N., Fabries, J., Ferguson, A.K., Ginzburg, I.V., Ross, M., Seifert, F.A., Zussman, J., Aoki, K., Gottardi, G. (1988) Nomenclature of pyroxenes. *Mineral. Petrol* 39, 55-76.
- Orlandini, P. (1954) Le nuove antefisse sileniche e il loro contributo alla conoscenza della coroplastica siceliota. *Archeologia Classica* VI, 251-266.
- Orlandini, P. (1956) Altre antefisse sileniche di Gela. *Archeologia Classica* VIII, 47.
- Orlandini, P. (1958) Nuovi acroteri a forma di cavallo e cavaliere dall'acropoli di Gela, in: *Scritti in onore di Guido Libertini*, Olschki, L.S., (Ed.), Firenze, pp. 117-128.
- Orlandini, P. (1968) Topografia dei santuari e documentazione archeologica dei culti. *Rivista dell'Istituto di Archeologia e Storia dell'Arte* XV, 20-66.
- Rescigno, C., Sampaolo, V. (2005) Appunti sull'impiego del colore sulle terrecotte architettoniche capuane. *Mediterranea* II, 133-163.
- Riccardi, M.P., Messiga, B., Duminuco, P. (1999) An approach to the dynamics of clay firing. *Appl Clay Sci.* 15, 393-409.
- Schleif, H., Süsserott, H.K. (1944) Grossgriechische Dachterrakotten. *Das Schatzhaus von Gela. Olympische Forschungen* I, 83-110.
- Sepúlveda, M., Gutiérrez, S., Vallette, M.C., Standen, V.G., Arriaza, B.T., Cárcamo-Vega, J.J. (2015) Micro-Raman spectral identification of manganese oxides black pigments in an archaeological context in Northern Chile. *Heritage Science* 3, 1-6.
- Sguaitamatti, M. (1984) L'offrande de porcelaine dans la coroplastie gélaïenne. Mainz am Rhein.
- Spagnolo, G. (2000) Le terrecotte figurate dall'area della stazione vecchia di Gela e i problemi della coroplastica gela nel V sec. a.C.. *Quaderni di Archeologia Università di Messina* 1, 179-207.
- Thio-Henestrosa, S., Martín-Fernández, J.A. (2005) Dealing with compositional data: the freeware CoDaPack. *Math Geol.* 37, 773-93.
- Uhlenbrock, J. P. (1988) The Terracotta Protomai from Gela. A Discussion of Local Style in Archaic Sicily, Roma.
- Whitbread, I. K. (1995) Greek Transport Amphorae: A Petrological and Archaeological Study, Fitch Laboratory Occasional Paper, 4, The British School at Athens.
- Wikander, Ch. (1986) Sicilian Architectural Terracottas. A Reappraisal, Stockholm.
- Winter, N. (1993) Greek Architectural Terracottas from the Prehistoric to the End of the Archaic Period, Oxford.
- Zoppi, A., Lofrumento, C., Castellucci, E.M., Sciau, P. (2008) Al-for-Fe substitution in hematite: the effect of low Al concentrations in the Raman spectrum of Fe<sub>2</sub>O<sub>3</sub>. *Journal of Raman Spectroscopy* 39, 40-46.